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Philippe Menini, F. Parret, M. Guerrero, A. Martinez, K. Soulantika, et al.. Influence of Humidity on the CO Sensitivity of a New Gas Sensor Based on SnO2 Nanoparticles Surface-Doped with Palladium and Platinum. Eurosensors XVII, Sep 2003, Guimaraes, Portugal. pp.873. hal-02160594

HAL Id: hal-02160594
https://laas.hal.science/hal-02160594

Submitted on 19 Jun 2019

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Influence of Humidity on the CO Sensitivity of a New Gas Sensor Based on SnO_2 Nanoparticles Surface-Doped with Palladium and Platinum

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Summary: *In this paper, we show the influence of two doping agents Palladium and Platinum on the sensitivity for CO sensing of the nanoparticular SnO_2 sensors at an operating temperature of 450°C. It is well known that the evolution of the conductance of the sensitive layer is largely modified by doping. A study carried out to measure the influence of humidity demonstrates that if un-doped sensors show a variation of same sign but less important than in dry air, doped sensors display a very different behavior. Indeed, we obtain a point of null sensitivity between 0 and 10%RH (RH = relative humidity) and a strong inverse sensitivity above 15% RH. These results demonstrate the presence of unexpectedly different chemical operating modes for CO sensing according to the rate of humidity.*

Keywords: *gas sensors, SnO_2, nanoparticles, doping, sensitivity.*
Category: 5

1 Introduction

At present time, most of the gas sensors are either electrochemical or metal-oxide semiconductors in thick-film [1] or in thin-film [2] technology. The main problems of these techniques are : moderate level of sensitivity, low reproducibility, low selectivity, long stabilization periods and high power consumption for the thick layer. However, the sensor technology has integrated for a few years the development of nanomaterials.

This article deals with a new generation of nanoparticular SnO_2 gas sensors (Fig. 1). This new technology allows a very high surface-on-volume ratio and then may display a high level of sensitivity due to the reduction of grain size in agreement with Yamazoe et al.[3].

However different aspects of this kind of sensors have to be studied to acquire the sensing principles and to improve their actual performances.

A new technical method has been achieved to obtain a surface doping with nanocrystals of PdO and PtO_2 fixed on the tin oxide nanoparticles [4-5]. Electrical characterization under CO of these new sensors should produce a comparison of sensors' sensitivities according to the different doping agents. Then, the influence of moisture will be discussed.

2 Description of the sensor

The sensor used in this study is formed by a microhotplate platform and a nanoparticular SnO_2 sensing layer. The microhotplate architecture was initially developed for Motorola and presently exploited by Microchemical Sensors S.A. A SiO_xN_y membrane of 2 µm of thickness supports a polysilicon heater of 600µm x 430µm. Dimensions have been optimised to achieve good thermo-mechanical reliability and good homogeneity of temperature on the active area. The heater can reach temperatures of 500°C with a power consumption lower than 100mW.

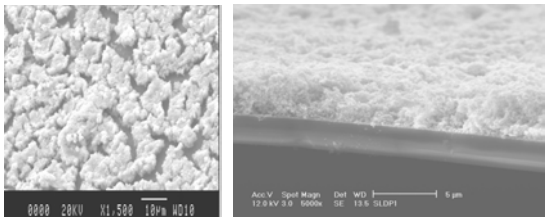


Fig. 1. SEM images of the sensing layer.

The metal-oxide used in this sensor is a crystalline SnO_2 nanomaterial synthesized by the decomposition and oxidation of a tin based organometallic precursor ($[Sn(NMe_2)_2]_2$), the mean grain size obtained is 15 nm of diameter. Doping is achieved by decomposing an organometallic precursor $M(dba)_2$ (M=Pd, Pt; dba = dibenzyli-deneacetone) under dihydrogen at the surface of the tin/tin oxide preformed particles. Upon heating in situ on the platform the tin material is transformed into SnO_2, whereas the doping agents are oxidized into PdO and PtO_2 nanocrystals which mostly remain at the surface of tin (Fig. 2). This material is then deposited using a microinjector technique over the two electrodes placed in the homogeneous temperature region of the heater. This heater permits the full oxidation into SnO2 with a controlled temperature cycle from ambiant to 500°C.

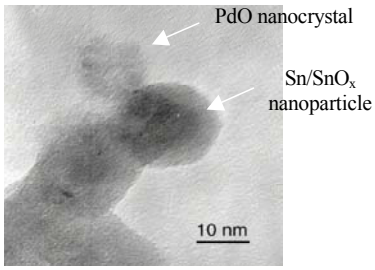


Fig. 2. HRTEM image of the Pd-doped SnO_2.

3 Experimental results

The experimental set-up consists of a gas delivery system, an exposure glass vessel and an electronic circuit for resistance determination through voltage measurements.

Before any test sequences, all sensors have to be subjected to several heating cycles in dry air.

The optimal operating temperature has been determined near 450°C for all tested sensors under 500ppm of CO. But, this temperature must not be exceeded to avoid electromigration problems from contact pads metal through polysilicon layer.

The sensitivity of the sensor is determined by $S = (R_{gas}-R_o)/R_o$ where R_o is the sensitive layer resistance without CO and R_{gas} the resistance measured under CO.

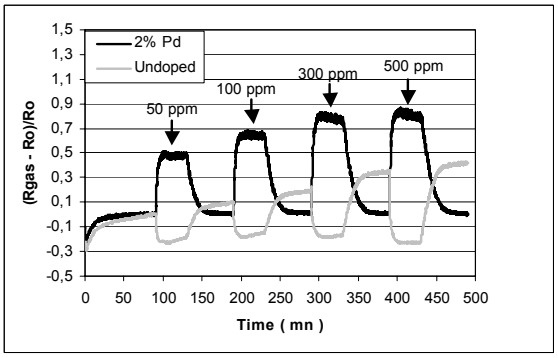


Fig. 3 : Undoped and Pd-doped sensor responses under CO injections in dry air.

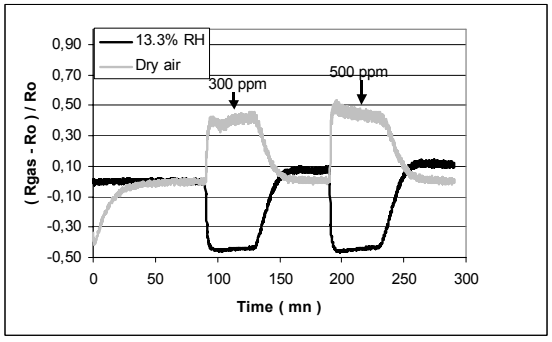


Fig.4 : Exemple of Pd-doped sensor responses in dry and humid atmosphere.

In figures 3 and 4 it can be seen that the response of doped sensors in humid air is inversed compared to that one in dry air. Secondly, doped and undoped sensors display the same variation (in term of sign) in humid atmosphere as it is observed in literature.

So, the doped-sensor sensitivity is null for a relative humidity about 5%.

4 Discussion

This inversion of sensitivity is surprising and, to the best of our knowledge unprecedented. The correlation with the rate of humidity is clear and the observation of a point of zero sensitivity confirms it. The origin of this behavior is as yet unclear but probably results from different catalytic properties of the doping nanoparticles according to the presence of humidity. The surface chemistry of this system has therefore to be studied in detail. An hypothesis would be the variation of rates of CO oxidation on the catalyst and absorption on SnO_2 according to the rate of humidity.

5 Conclusion

A new generation of gas sensors based on nanoparticular SnO_2 sensitive layer with two doping catalysts - Palladium and Platinum - has been elaborated and tested. The maximal sensitivity to carbon monoxide has been obtained at the upper temperature 450°C for all of the sensors. First results in dry air reveal that the palladium is the best doping agent for CO detection, but, at the moment, that in wet ambiant air, the best sensitivity is achieved for a Pt-doped sensor in agreement with the litterature [6].

The inversion of sensitivity from dry to wet air introduces firstly, a new concept of electrochemical operating mode between oxygenated gases and the superficially doped sensing layer and secondly, an opportunity to increase the selectivity using a sensor array.

Acknowledgments

Authors would like to thank Mr. P. Fau of Microchemical Systems S.A. which have provided us the micromachined platforms.

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